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Changes in Certain Properties of Grey Forest Soil Polluted with Emissions from a Copper-smelting Plant

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Abstract—The influence of heavy metals in combination with sulfurous anhydride on grey forest soil of the southern taiga caused retardation of the decomposition of active litterfall fractions, disruption of the soil structure, and the development of gleying. These changes were found at the morphological level (formation of thick specific organogenic horizons, a decrease in the degree of soil aggregation, the frontal flow of humus, development of the greyish-blue layer of the profile, and the presence of many iron concretions), the physicochemical level (a decrease in the metabolic calcium content, an increase in actual and hydrolytic acidity), and the biochemical level (a decrease in the rate of the decomposition of cellulose and urea).

INTRODUCTION

In field investigations of territory exposed to chemical pollution, the soil is often regarded only as the location of pollutants or the habitat of pedobionts, which are used as sensitive indicators of technogenic load. Less attention is given to analysis of the properties of soil under environmental pollution from the actual sources of the emissions. The processes of the accumulation and migration of pollutants and certain parameters of the absorption complex are exceptions to the general rule (Doncheva, 1978; Il'in, 1991; Chertov, 1990; Chertov *et al.*, 1990; Romashkevich and Obukhov, 1991; Lukina and Nikonov, 1995). The influence of pollutants on soil characteristics, especially with respect to the excessive input of acidic agents, was studied at greater length in laboratory and field experiments (Bache, 1980; Greszta *et al.*, 1987; Florinskii and Sedova, 1992). However, due to the scarcity of information, especially from field observations, such questions as the determination of the direction of fundamental pedogenic processes under technogenic contamination and the scale and schedule of changes in the properties of soil remain open.

New classifications of soils transformed by technogenic contamination were recently suggested (Gennadiev *et al.*, 1992; Lebedeva *et al.*, 1993; Solntseva *et al.*, 1990; Sokolov, 1991). Among these, chemically polluted soils are the most complicated and least studied. Therefore, the establishment of diagnostic criteria for such soils on the basis of data from the investigation of the entire diversity of soil transformation processes is of current interest.

We studied the influence of powerful flows of pollutants (heavy metals in combination with sulfurous anhydride) from a localized source of emission (a copper-smelting plant) that had been functioning for a long time on grey forest soils of the southern taiga. The selection of the type of contamination was not random. This pollution acidifies soil solutions, causing an increase in the mobility of heavy metals and, as a result, their toxicity to biota. The latter has highly negative consequences for forest ecosystems, which completely degrade at high levels of contamination. Thus, regularities of changes in the soil can be found much more easily for the selected type of chemical pollution than for others.

The present work is part of a series of comprehensive studies on the condition of forest ecosystems conducted in the region under the influence of the factory being investigated. Some of the results of these studies have been published (Vorobeichik *et al.*, 1994; Vorobeichik and Khantemirova, 1994; Vorobeichik, 1995). Analysis of soil characteristics allowed us, on the one hand, to supplement the picture of the response of ecosystems to pollution and, on the other hand, to compare the extent of the transformation of the soil with that of other components of the ecosystem.

REGION UNDER INVESTIGATION

This study was conducted on the territory to the west of the Sredneural'skii copper-smelting plant (upwind from the plant). The plant is located on the outskirts of the town of Revda, Sverdlovskaya oblast. Along the selected direction, the technogenic desert extended 0.5–1 km from the plant limits, the impact zone, 2–3 km, and the buffer zone, 6–7 km. The control area was located 20–30 km from the plant. Table 1 shows the magnitudes of the influx and deposition of heavy metals in the specified zones.

Five key plots were laid down within the technogenic desert (0.5 km from the plant), the impact zone (2 km), the buffer zone (4 and 7 km), and the background territory (30 km) in trans-accumulative land-

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scapes (the lower part of slopes), where, under a canopy of spruce–fir forest of various associations, grey forest soils are predominant. Earlier, we described the character of the technogenic changes in the vegetation in this region (Vorobeichik *et al.*, 1994; Vorobeichik and Khantemirova, 1994). Before the plant began working (1940), the key plots supposedly had similar soil and vegetational cover.

METHODS

In July 1994 and July and August of 1995, we established five full-profile soil pits (sampling of the genetic horizons was performed in 1994). These years differed in their humidity: the total amount of liquid precipitation during spring and summer was greater than average in 1994 and less than average in 1995.

The content of metabolic calcium and magnesium was determined by the trilonometrical method. Hydrolytic acidity was determined according to Kappen (*Practical Course* …, 1989), and pH_{water} was measured ionometrically in preliminary dried specimens (at a substrate–water ratio of 1 : 5). Concentrations of mobile forms of heavy metals (Cu, Pb, Cd, Zn) in the upper (0–5 cm) layer of the humus–accumulative horizon were measured in acid extracts (with 5% HNO_3 at a substrate–extractant ratio of 1 : 5 for 24 hours) on an AAS-3 atom-adsorption spectrometer (Karl Zeiss).

The rate of the destruction of pure cellulose was determined by the application method (*Practical Course* …, 1989) in fresh specimens of the organogenic and humus–accumulative horizons according to the loss of air-dry mass of filter paper under optimal hydrothermal conditions (25°C, maximum water-holding capacity). The time of exposure was 31 days. The urea decomposition rate was measured by the quick test (Aristovskaya and Chugunova, 1989) in the same specimens under analogous conditions according to the intensity of ammonia production (expressed in terms of variation in pH).

RESULTS

The differentiation of the soil profile into genetic horizons typical of grey forest soils of the Ural region (Firsova *et al.*, 1982, 1990) remained unchanged in all zones of pollution (see figure). The macroaggregate composition of the mineral part of the profile was almost invariable. Only the degree of distinction of this part of the profile varied. In fact, loose nuciform structure, cloddy structure, and blocky–cloddy structure of aggregates predominated at horizons B1gh, B2gh, and BCg in the impact zone, while fine nuciform structure, nuciform structure, and prismatic nuciform structure predominated in the background territory. The change in texture was more pronounced in the humus–accumulative horizons. The granular and cloddy–granular soil structure in the background territory was replaced by dusty–granular, dusty, and dusty–cloddy structures in the impact zone. The character of humus flow varied over the contaminated territory: in the zone of technogenic desert, humus flowed with a wide leading edge with separate darker tongues at places, whereas, in the buffer (7 km) and background zones, it flowed with tongues and pockets.

The affected soils differed in the color of contanes (skins) in the mineral horizons. These distinctions were especially clearly defined in the year with a large amount of precipitation: while the bluish and bluish-grey contanes were present at all mineral horizons at

Table 1. Minimum (min) and maximum (max) values of the input and deposition of pollutants in different zones

Parameter	Zone					
	background		buffer		impact	
	min	max	min	max	min	max
Precipitation on 1 m^2 per year, mg:						
Cu	39.65	92.63	66.46	236.81	125.67	1043.80
Pb	8.82	27.75	13.77	44.50	34.60	243.74
Cd	0.59	2.40	0.83	3.48	1.90	12.98
Zn	41.14	153.20	69.28	156.31	125.84	443.34
mineral particles, g	1.70	7.51	2.81	9.63	4.58	26.32
Concentration in horizon A1, mg/kg:						
Cu	32.48	71.18	114.59	422.03	396.28	596.38
Pb	21.94	37.44	22.16	180.36	95.96	265.39
Cd	0.84	1.55	1.80	6.91	2.74	10.02
Zn	35.67	60.27	64.00	91.95	72.83	91.11
pH_{water} in horizon A1	5.04	6.24	4.48	5.77	4.37	5.17

distances of 0.5, 2, and 4 km from the plant, greyish-brown contanes and pale yellowish-brown powderings were located 7 and 30 km from the plant. In the dry year, the mineral part of the soil profile in the impact zone and technogenic desert was marked by diverse tints of greyish-brown; the horizons A1Bh and B1h had whitish colors and were significantly lighter in color than the buffer and background zones. In the year with excessive precipitation, aggregations of very loose (from 4 to 7 mm in diameter) ocherous concretions were observed in the mineral horizons of the polluted soil. In the dry year, the concretions were dense (from 2 to 3 mm in diameter) and brown.

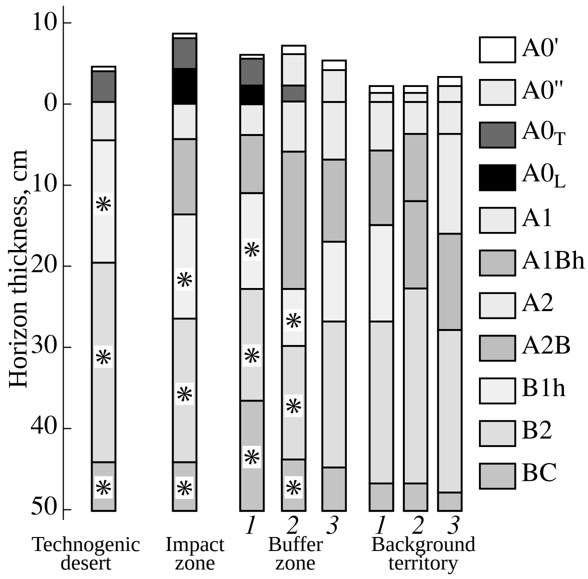
The organogenic horizons changed to a greater extent than the mineral part of soil profile. In the technogenic desert, the organogenic horizon was extremely different from the typical litter of grey forest soil. This horizon represented cohesive dense peatlike moss coverage $A0_T$ with high moisture capacity and was composed of living and dead tissues of the moss *Pohlia nutans* (figure). The thickness of this coverage ranged from 3 to 5 cm. The transition from layer $A0_T$ to layer A1 was very sharp. The horizon $A0_T$ was absent in part of the technogenic desert, as the upper horizons down to the B horizons were mechanically removed or washed away.

The organogenic horizons in the impact zone were represented by moss coverage $A0_T$ (from 3 to 5 cm thick) and, situated below, the horizon $A0_L$ comprising needle and leaf–needle litter (from 2 to 3 cm thick) almost completely retaining its primary structure. In microdepressions, "burials" of undecomposed wood and herb litter up to 10–15 cm thick were observed. On part of the territory, the layer $A0_T$ was absent, and litter formed a thick (usually 6–8 cm, but up to 10–11 cm) horizon$A0_L$.

At a distance of 4 km from the plant, two different states of organogenic horizons were found. In addition to the horizons $A0_T$ and $A0_L$ marked in the impact zone, sodded litter 4–6 cm thick, similar in structure to typical litter, was often observed here. Litter 5–6 cm thick, typical of grey forest soil (Firsova *et al.*, 1982, 1990) and differentiated into three horizons (the leaf, fermentative, and humus–compost horizons), was formed at a distance of 7 km from the plant.

The structure of litter in the background territory also differed from the typical structure: its thickness barely reached 1 cm, the fermentative horizon was not clearly defined, and the leaf horizon lay directly over the humus–compost horizon. The litter was very friable ("cobweblike") and rarely interlaced with roots. By the middle or end of summer, the leaf horizon sometimes completely disappeared in forest stand clearings.

As the plant is approached, the degree of saturation with bases decreased 1.5 times in comparison with the background level at the organogenic horizon and 1.3 times at the humus–accumulative horizon (Table 2). This can be accounted for by a decrease in the content



Scheme of the morphological organization of the soil profile in different zones: (*1–3*) variants of soil within one zone; (*) presence of features of gleying.

of metabolic calcium (by 3.2 times at the organogenic horizon and 1.3 times at the humus–accumulative horizon) as well as an increase in hydrolytic acidity (by 1.3 and 2 times, respectively). The magnesium content was nearly constant in all zones.

In the technogenic desert, the rate of the decomposition of urea decreased only 2.5–3 times at the organogenic horizon, whereas, at the humus–accumulative horizon, it decreased 15 times (Table 3). Conversely, the rate of the decomposition of cellulose was considerably lower at the organogenic horizon and was almost equal to zero in various areas of the technogenic desert. At the humus–accumulative horizon, this parameter decreased 6.5 times. Note that the peak of cellulase activity was observed in the buried horizon of polluted soil $A0_L$, and that this activity was 2.8–4.8 times higher than in the neighboring horizons $A0_T$ and A1. This was most pronounced in the impact zone. At a distance of 4 km from the plant, a higher rate of the decomposition of cellulose in layer $A0_L$ was found in only two out of five cases.

DISCUSSION

The morphology of the soil profile, as a concentrated reflection of soil genesis, is of paramount importance for soil diagnostics (Rozanov, 1975). However, changes in soil morphology under chemical contamination were only noted in a few works[1]. For example, Romashkevich and Obukhova (1991), investigating the same region, did not find any changes in soil morphol-

[1] Except in cases of heavy ashfall of calcium-containing emissions and coal dust (Rusanova, 1995) or oil spills (Solntseva *et al.*, 1990; Gennadiev *et al.*, 1992).

ogy. At the same time, such changes enable the systematization of chemically polluted soils according to the degree of pollution as well as a genetic–substantive basis.

The weak resolution of field description presents the main difficulty in detecting changes in the morphological parameters of soil. In spite of this, we characterized polluted soil differing from normal soil organization according to a number of important features. Three groups of features, each indicating that a certain transformative process caused by the technogenic load (inhibition of the decomposition of organic matter, destruction of the soil aggregate structure, or the development of gleying) is taking place, can be identified. The characteristic properties of these groups of features at the level of the morphology of the soil profile are confirmed by changes in physicochemical and biochemical parameters.

The formation of the specific peatlike and buried-leaf horizons $A0_T$ and $A0_L$ in the affected area and the corresponding two- to threefold increase in litter thickness (figure) are outward manifestations of the almost complete inhibition of the decomposition of the active litter fractions in the forest ecosystem. Direct measurements of the parameters of soil biological activity confirm the fact that the soil saprophilous complex, including cellulose-decomposing and ammonificating microorganisms, was suppressed (Table 3). The considerable

Table 2. Basic parameters of the soil absorption complex and hydrolytic acidity in different zones (average values; minimum and maximum values are given in parentheses)

Load zone and distance from the factory, km	Horizon	Content of metabolic bases, mg · eq /100 g of soil		Hydrolytic acidity, mg · eq /100 g of soil	Degree of saturation by bases, %
		Ca	Mg		
Technogenic desert, 1	$A0_T$	14.0 (12.0–18.0)	4.4 (4.0–6.0)	15.8 (11.9–18.0)	53
	A1	10.3 (7.0–13.6)	3.8 (2.6–4.8)	10.4 (8.4–11.4)	57
Impact, 2	$A0_T$	18.8 (12.0–24.0)	5.6 (4.0–10.0)	15.6 (13.0–20.3)	61
	$A0_L$	18.6 (14.0–20.0)	6.7 (6.0–8.0)	13.6 (12.6–14.9)	64
	A1	12.7 (10.4–14.0)	3.3 (2.4–4.8)	8.5 (8.1–8.9)	64
Buffer, 4	$A0_T$	31.0 (28.0–36.0)	6.7 (6.0–8.0)	14.7 (8.8–15.2)	76
	$A0_L$	22.0 (17.6–30.0)	7.0 (4.0–14.0)	14.2 (13.3–15.8)	72
	A1	15.8 (11.4–18.2)	4.9 (3.6–8.0)	10.0 (7.5–12.3)	69
Buffer, 7	A0"	40.0 (36.0–52.0)	13.2 (6.0–22.0)	11.3 (7.4–14.4)	82
	A1	9.0 (6.2–14.4)	4.2 (2.8–5.2)	6.3 (5.3–7.9)	68
Background, 30	A0"	45.2 (38.0–56.0)	8.8 (8.0–10.0)	11.3 (9.8–12.6)	82
	A1	13.2 (7.6–18.2)	3.8 (3.2–5.6)	5.4 (4.9–6.3)	75

Table 3. Parameters of soil biological activity in different zones (average values; minimum and maximum values are given in parentheses)

Load zone and distance from the factory, km	Horizon	Rate of decomposition	
		urea, units of pH/hour	cellulose, %/day
Technogenic desert, 1	$A0_T$	0.350 (0.240–0.460)	0.000 (0.000–0.001)
	A1	0.010 (0.001–0.034)	0.101 (0.002–0.485)
Impact, 2	$A0_T$	0.750 (0.300–0.810)	0.241 (0.000–0.571)
	$A0_L$	0.120 (0.067–0.180)	0.686 (0.201–1.377)
	A1	0.071 (0.057–0.095)	0.141 (0.001–0.235)
Buffer, 4	$A0_T$	0.550 (0.350–0.710)	0.405 (0.001–0.910)
	$A0_L$	0.156 (0.120–0.190)	0.209 (0.160–0.190)
	A1	0.062 (0.018–0.097)	0.067 (0.001–0.216)
Buffer, 7	A0"	0.432 (0.170–0.810)	0.946 (0.015–2.350)
	A1	0.108 (0.053–0.150)	0.238 (0.067–0.710)
Background, 30	A0"	0.940 (0.530–1.200)	1.290 (0.020–1.912)
	A1	0.154 (0.089–0.300)	0.641 (0.026–1.041)

decrease in the number of primary decomposers of organic matter—saprophages of the mesofauna and especially eathworms—and their subsequent elimination were detected earlier on the polluted territory (Vorobeichik *et al.*, 1994; Vorobeichik, 1995).

The high activity of decomposition in the forest litter and the decrease in litter thickness observed in the background territory are probably connected with the "fertilizing" influence of low concentrations of heavy metals on microorganisms (Babich and Stotzky, 1985; Kobzev, 1980). In addition, the great number of earthworms in the background territory (Vorobeichik *et al.*, 1994) was probably associated with optimal hydrothermal conditions in certain periods.

It is rather interesting that the vertical decrease in the cellulose decomposition rate was irregular in the impact zone. Values of the rate in the buried horizon $A0_L$ were close to the values in the background territory and were greater than that in the neighboring horizons. This fact attests to the existence of microzones with high microfaunal activity. The sharp increase in the horizontal heterogeneity of the decomposition rate, related to the differentiation into biotopes with low and high biological activity, was noted earlier in the impact zone (Bezel' *et al.*, 1994).

The second group of features closely related to the organization of the profile of chemically polluted soils indicates destructurization of the humus–accumulative horizon and, to a lesser degree, the underlying mineral horizons. The destruction of soil aggregates was especially clearly defined in the soil of the technogenic desert, which exhibited thixotropy during the period of intense rainfall. This can be regarded as an example of combining the properties of systematically different soils in one profile due to technopedogenesis (Solntseva *et al.*, 1990). Most likely, the observed morphological deviations are caused by changes in the absorption complex of the soil. The decrease in the biogenic accumulation of calcium and magnesium due to the depression of herbaceous vegetation, the higher intake of calcium by the soil absorption complex following suppression of organic matter mineralization, and the acid leaching of calcium and magnesium from the upper horizons (Table 2) result in the replacement of these elements by hydrogen and aluminium ions. The aforementioned processes are evidenced by increases in actual (Table 1) and hydrolytic (Table 2) acidity and the reduced structurization of soil in the affected area. The excess of sulfate ions and high concentrations of mobile forms of copper (Table 1) can also influence the state of the soil absorption complex and, hence, the aggregate structure. The disruption of soil structure is probably related, to some degree, to inhibition of the activity of soil microorganisms (Vorobeichik *et al.*, 1994) that play an important role in forming and maintaining the stability of small and large aggregates by means of polysaccharide excretion and filament formation (Wood, 1991).

Finally, the third group of morphological features of polluted soil (changes in the color of contanes and the character of humus flow) indicate the development of gleying. In addition to the aforementioned features, changes in the ground vegetation (replacement of nemoral–wood sorrel associations by grass–horsetail and moss–horsetail associations) attest to higher hydromorphism in the impact zone. The disturbance of hydrology in the polluted territory can apparently be explained as follows. A decrease in desiccation due to tree stand destruction forms a water-resistant illuvial horizon, disturbing geochemical processes in the slope soil due to the backing up of the ground–subsoil water by engineering projects. Further investigations are necessary to estimate the relative contributions of these factors. However, we believe the first factor exerts the greatest influence. It is well known that the increase in the flooding of mineral horizons after the complete felling of forests (Huhta *et al.*, 1967) can result in the development of gleying (Dedkov *et al.*, 1987). In the present case, felling can be regarded as analogous to the depression and destruction of the tree stand. It is interesting that the contamination of tundra soil by calcium-containing dust leads to the reverse process—the disappearance of the morphological features of gleying—caused by the replacement of acidophilous vegetation with high moisture-absorbing capacity by calciophilous vegetation with low moisture-absorbing capacity (Rusanova, 1995).

Under conditions of high hydromorphism, gleying may be related to specific chemical reactions involving certain components of emissions. Thus, the formation of anaerobic zones is probably caused by the high intake of oxygen from liquid precipitation and the soil solution in the process of the oxidation of sulfurous anhydride to sulfate (Nikoladze, 1989). A decrease in the oxygen content in the soil solution may also be related to the oxidation of iron compounds introduced by dust particles.[2] These mechanisms can only work under excessive moistening of all soil horizons; during drought, they are blocked by free access to oxygen.

As to the characteristic times of changes in the soil parameters, it should be stressed that the studied territory was exposed to strong technogenic influence over a long period (more than 50 years). Therefore, it is quite likely that we are observing not the process of transformation, but the results of this process. Since we have data from a one-time survey obtained at the end of the period of pollution, the rates of changes can only be speculatively evaluated by means of the principle of spatial–temporal analogies.

Among the studied parameters, the traditional soil-moment parameters (the structure of organogenic horizons, the condition of the soil absorption complex, bio-

[2] According to analysis of the contamination of the snow cover, iron (the sum of acid- and water-soluble forms) fallout was 10–20 times more intensive in the impact zone than in the background territory (Polents and Bel'skii, 1991).

logical activity) were changed, as expected, to a maximum degree on the polluted territory. They begin to vary first (in the buffer zone), while the characteristics of the arboreous and herb–dwarf shrub layer remain unchanged under the same technogenic load (Vorobeichik *et al.*, 1994).

In addition, contamination causes changes in the more conservative soil-memory parameters (aggregate composition, differentiation of the profile according to the content of humus and silt). However, their variation can only be detected at higher contamination levels (in the impact zone and technogenic desert), when other components of the ecosystem completely degrade. Therefore, the labile parameters of the soil change almost in parallel with the transformation of biota, while the conservative characteristics considerably lag. At the same time, under natural conditions, change in soil-memory parameters takes more time, on the order of hundreds and thousands of years (Targul'yan and Sokolov, 1978). Their variation over the period of the operation of the factory indicates the magnitude of the technogenic load as well as its specifics in relation to natural factors.

It is essential to stress that all these technogenic changes in soil characteristics have natural analogies. To speak, for example, about "technogenic gleying" or "technogenic inhibition of destruction" is possible only in the sense that these phenomena were caused by the flux of pollutants and the subsequent transformation of biota and inorganic components, and, without pollution, these processes would not take place in these biotopes. There is no fundamental difference between "technogenic" features and their "natural" analogs in their substantive manifestation. This is one of the difficulties of the diagnostics of technogenic modifications of soil, since we can only draw a conclusion about the "unnaturalness" of modification when certain features are present in unusual combinations or are detected in atypical biotopes.

CONCLUSION

The reaction of soil to contamination was studied at three levels of organization: morphological, biochemical, and physicochemical. Technogenic changes in biochemical and physicochemical parameters are reflected in the morphological appearance of soil, influencing not only the soil-moment, but also, the soil-memory to some extent. The following are the basic features of soils exposed to technogenic pollution, which are easily recognizable in morphologial description: (a) increased thickness of the litter comprising the specific peatlike horizon $A0_T$ and buried leaf horizon $A0_L$, (b) destruction of humus–accumulative horizons, and (c) gleying of mineral horizons, as determined by the bluish-grey layer of the profile and frontal humus flow. These features are diagnostic for soil units that were transformed from the original grey forest soil of the southern taiga by extensive pollution with heavy metals in combination with sulfurous anhydride. Therefore, the term "technogenic" can be applied to each of these features (technogenic litter, technogenic destruction, and technogenic gleying).

The studied changes in the soil undoubtedly have negative consequences for the functioning of forest ecosystems. Inhibition of the decomposition of organic matter, changes in soil structure, and the formation of anaerobic zones diminish soil fertility. These processes, in combination with the high toxicity of the soil, decrease the total productivity and stability of biota.

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